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ABSTRACT

In polyethylene microencapsulation, low-level mixed waste (LLMW) is homogenized with molten polyethylene and extruded into containers, resulting in a lighter, lower-volume waste form than cementation and grout methods produce. Additionally, the polyethylene-based waste form solidifies by cooling, with no risk of the waste interfering with cure, as may occur with cementation and grout processes.

We have demonstrated real-time monitoring of the polyethylene encapsulation process stream using a noncontact device based on transient infrared spectroscopy (TIRS). TIRS can acquire mid-infrared spectra from solid or viscous liquid process streams, such as the molten, waste-loaded polyethylene stream that exits the microencapsulation extruder. The waste loading in the stream was determined from the TIRS spectra using partial least squares techniques. The monitor has been demonstrated during the polyethylene microencapsulation of nitrate-salt LLMW and its surrogate, molten salt oxidation LLMW and its surrogate, and flyash. The monitor typically achieved a standard error of prediction for the waste loading of about 1% by weight with an analysis time under 1 minute.

INTRODUCTION

The U. S. Department of Energy has large amounts of low-level mixed waste (LLMW) powders, such as salts and flyash, which must be converted into stable waste forms prior to long-term storage. Polyethylene microencapsulation produces a smaller and lighter immobilized waste form than the cementation processes commonly in use (1-4). Microencapsulation also avoids the chemical interactions with the waste that create cure problems for cementation. Polyethylene microencapsulation is well suited for on-line monitoring that could ensure the processed waste meets regulatory specifications.

The on-line microencapsulation processing monitor provides a continuous, real-time, quantitative record of the waste-loading concentration in the polyethylene matrix. This aids the process operators in developing treatment protocols for specific wastes and allows them to maintain optimum processing during waste treatment. In addition, the monitor log can assist in waste certification and act as an archival record of the waste composition. The monitor we have developed uses transient infrared spectroscopy (TIRS) to perform its analysis. TIRS is a noncontact method for acquiring the mid-infrared spectrum of a moving stream of solid or viscous-liquid material. The stream composition is then derived from the spectrum using partial least squares analysis.

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On the microencapsulation process line, the monitor typically determines the waste loading every 15 to 60 seconds with an accuracy of about 1% by weight. The monitor has been demonstrated on lines encapsulating nitrate-salt LLMW and its surrogate (sodium nitrate), flyash, and molten-salt-oxidation LLMW (a mixture of sodium carbonate and sodium chloride). Demonstrations done at Rocky Flats Environmental Technology Site and Brookhaven National Laboratory are discussed in this paper. We have discussed elsewhere other demonstration analyses at Brookhaven (5, 6) and Rocky Flats (7).

TRANSIENT INFRARED SPECTROSCOPY

Spectroscopic analysis relies on the fact that sufficiently thin or dilute samples will absorb, emit, or reflect only those wavelengths that strongly interact with the molecules of the sample. The spectrum resulting from these interactions consists of a set of sharp features, called bands, that are characteristic of the particular molecules in the sample.

TIRS is a general molecular-analysis on-line monitor for use on process streams of solid and viscous-liquid materials. It has been demonstrated on a wide variety of materials, both in the laboratory (8, 9) and on process lines (5-7). Fig. 1 schematically shows how the TIRS monitor is applied to a waste-microencapsulation line. The molten stream of polyethylene-encapsulated waste flows through the field of view of an infrared spectrometer. The molten stream, being hot, strongly radiates in the mid-infrared part of the spectrum, which the spectrometer observes. This bulk emission is a blackbody spectrum; that is, it consists of emission at all wavelengths, and its intensity varies slowly with wavelength, following Planck's Law. This blackbody spectrum is indicative of the temperature of the stream, but it is not useful in analyzing the stream composition. It lacks the sharp bands spectroscopists rely on because the stream is too thick and optically opaque.

The TIRS monitor avoids this blackbody problem by focusing on only a thin surface layer of the stream. The TIRS monitor trains a small jet of room-temperature air onto the surface of the process stream as it flows past the spectrometer. This cools a thin surface layer of the stream. This surface layer no longer emits infrared radiation strongly because of its reduced temperature, but the infrared spectrometer still observes infrared radiation from the rest of the process stream. This radiation must pass through the cooled layer to reach the spectrometer, and the cooled layer absorbs some of it. The cooled layer is sufficiently thin that it absorbs only at its characteristic bands. The spectrometer therefore observes the smooth blackbody emission spectrum of the stream bulk with the sharply structured transmission spectrum of the cooled layer superimposed on it. The chemical analysis is based on the transmission spectrum.

For the analyses discussed here, a Bomem MB 100 FTIR spectrometer fitted with a mercury-cadmium-telluride detector was the infrared spectrometer around which the TIRS monitor was built. It operated at 8 cm^{-1} resolution. For the Figure 2 spectra, 100 scans were co-added, and 64 scans (requiring 55 seconds) were co-added for the data in Figures 3 and 4. For the early work illustrated in Figure 2, the TIRS cooling jet was an 8 L/min flow of helium cooled by passage through a liquid-nitrogen bath and delivered by a flat 0.7 mm by 5.5 mm nozzle. We later found that such a high level of cooling was not needed. For the analyses shown in Figures 3 and 4, the TIRS cooling jet was a 1.6 L/min flow of room-temperature air delivered by a length of 0.6 mm inner-diameter stainless-steel

tubing. The partial least squares analysis of the data was done with GRAMS PLSplus (Galactic Industries).

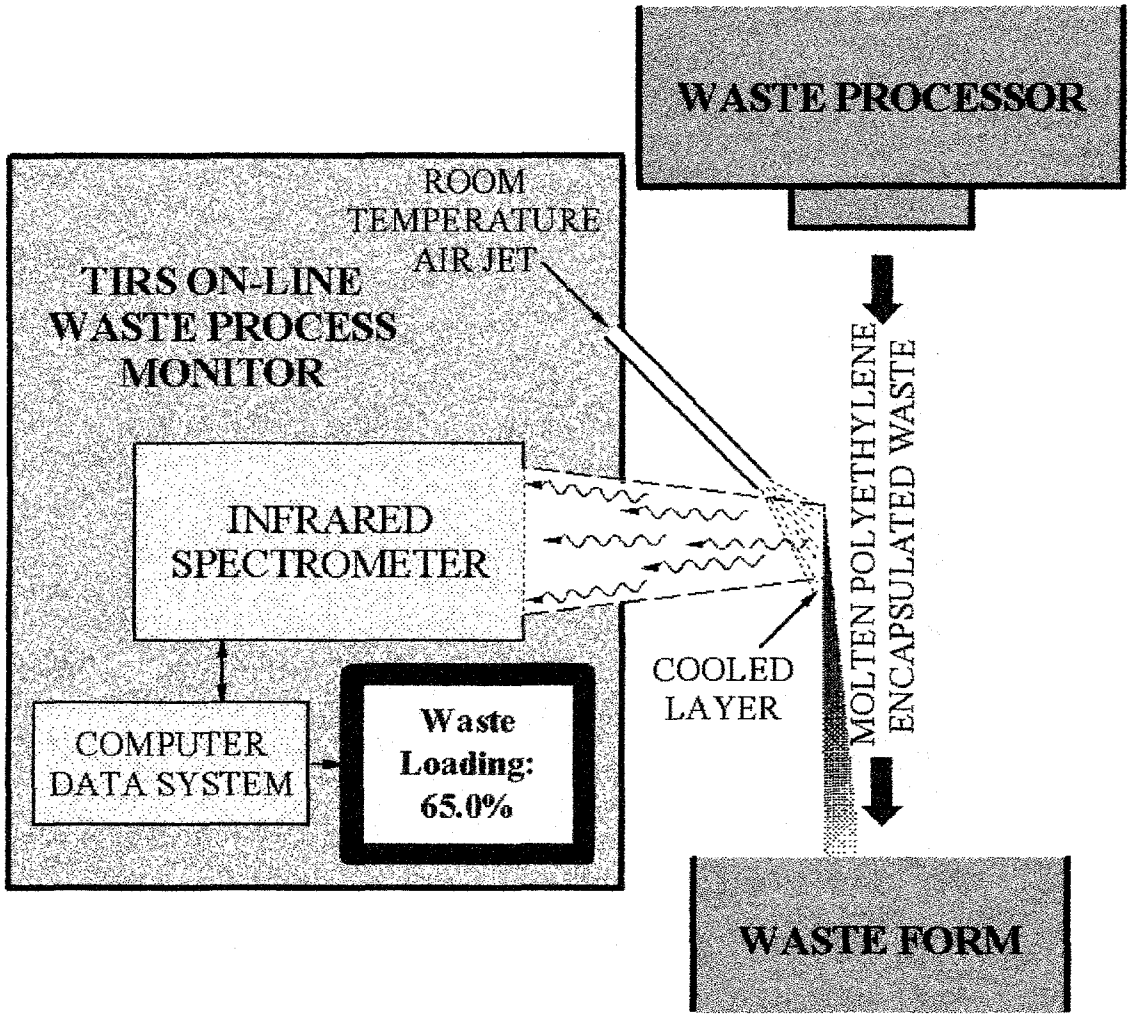

Fig. 1. Schematic of the TIRS Monitor on a Polyethylene-Encapsulation Process Line

The TIRS monitor can also be used with cool process streams (5, 8). In that case, the TIRS monitor uses a hot-gas jet to produce a thin, heated surface layer. The structured emission from the thin layer can then be analyzed in the same manner as the structured transmission spectrum of the cooled layer produced when a cooling jet is used. Early tests on applying TIRS to encapsulation examined both cooling-jet and heating-jet versions (6). Both versions gave good results, but the cooling version is simpler and slightly more stable, so it was selected for the applications discussed here.

DATA TREATMENT

Spectra acquired by the TIRS monitor are raw signal intensities observed as functions of wavenumber. Usually in spectroscopy, such spectra are *normalized* by ratioing them against a reference spectrum so as to remove any wavenumber-dependent variations in the spectrometer response. In TIRS, this

normalizing also removes the Planck's Law rise and fall of signal intensity with wavenumber that is characteristic of thermal emission. Fig. 2, discussed below, shows both raw and normalized versions of spectra. The reference spectra used were blackbody emission spectra observed from the process stream when the TIRS cooling jet was turned off. The analyses discussed here are based on normalized spectra. Although analyses can usually be done using raw spectra, normalization often results in improved accuracy.

Partial least squares was used to derive the stream composition from the spectra (10). The partial-least-squares method calibrates the monitor by building a model from a training set of spectra. For the work reported here, the monitor acquired the training-set spectra while the waste processor was held at a series of stream compositions with stream flow rate and other process parameters held fixed. The "actual" compositions used for calibration were calculated from the feed rates of polyethylene and of waste or surrogate into the extruder. A measure of the accuracy of the resulting calibration is the Standard Error of Prediction (SEP) produced by single-elimination cross validation. In a single-elimination cross validation, one of the training-set spectra is removed and a calibration is developed using only the remaining members of the set. The composition of the excluded member is then determined from this calibration. The excluded member is then put back in, a second member is taken out, a new calibration is developed, and the second member is analyzed. This process is repeated until all members of the training set have been excluded and analyzed. SEP is the root mean square of the deviations of the analyses from the known sample compositions. Once the calibration model is built, analysis of an unknown spectrum is very fast (under 1 second), so partial least squares is compatible with real-time analysis.

RESULTS AND DISCUSSION

Figure 2 shows spectra taken during an early test at Brookhaven National Laboratory of applying TIRS to microencapsulation. Sodium nitrate was used as a surrogate for nitrate salt LLMW. The sodium nitrate was mixed with polyethylene, heated, and extruded. The spectra are of the molten polymer/salt stream as it exits the extruder. The lower panel shows the raw spectra recorded by the TIRS monitor for three different concentrations of sodium nitrate in the stream (given as weight percent). They are essentially blackbody spectra with transmission spectra superimposed. The overall rise and fall of these spectra follow Planck's Law for blackbody emission. Superimposed on the smooth blackbody envelopes are the narrow absorption bands of polyethylene and sodium nitrate. The upper panel shows the same spectra after normalization, which corrects for the blackbody curves, leaving just the transmission spectra of the components. The features at 836, 1786, 2090, and 2430 cm^{-1} all belong to sodium nitrate and increase in size as the nitrate salt concentration increases. The bands at 720, 1302, 1366, 1466, 2850 and 2920 all arise from polyethylene and shrink as the salt concentration rises. More data from this test has been presented elsewhere (5, 6).

A test microencapsulation of molten-salt-oxidation waste performed at Rocky Flats Environmental Technology Site produced the data in Figure 3. The figure shows the results of a single-elimination cross validation done on the PLS training-set spectra, with the TIRS-PLS predicted waste loading plotted against the actual waste loading. PLS required only 2 factors to achieve the excellent fit to the ideal line shown ($r^2 = 0.9991$). The SEP is 0.23 weight percent.

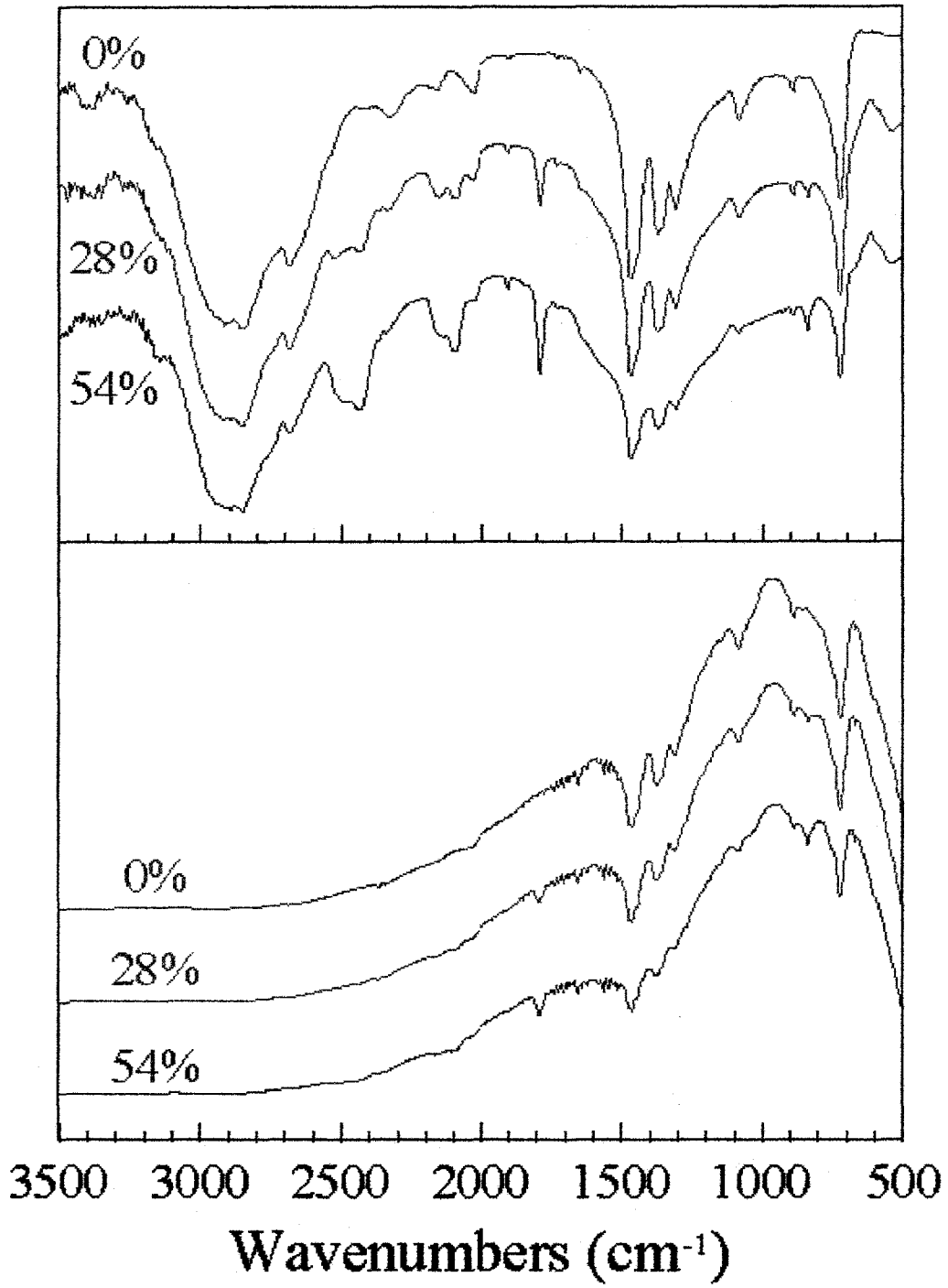

Fig. 2. TIRS spectra of a microencapsulation stream consisting of sodium nitrate in molten polyethylene. The bottom panel shows the raw spectra observed by the TIRS monitor, and the top panel shows the same spectra after normalization. The weight percent concentration of sodium nitrate is marked.

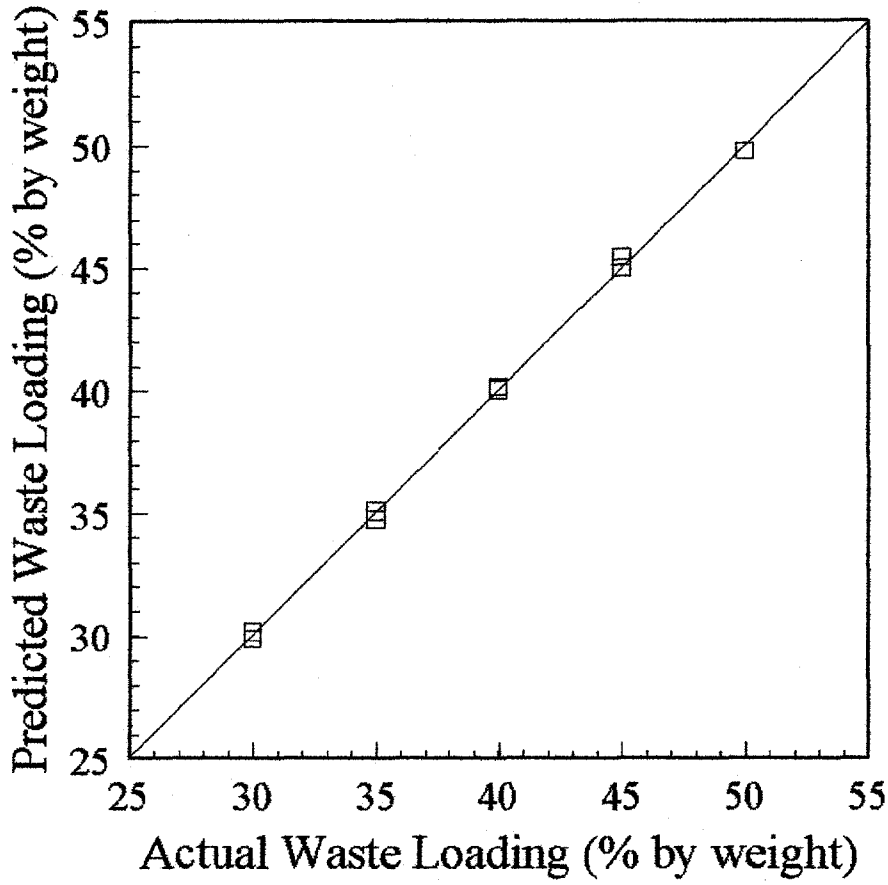

Fig. 3. Cross-validation correlation between TIRS-predicted process-stream composition and its actual composition during the microencapsulation of molten salt oxidation waste.

Figure 4 shows both the cross validation and the analysis of unknowns from a pair of tests at Rocky Flats. Here, separate microencapsulations were done on two different types of flyash, Class C and Class F (which differ in composition, principally by the presence of magnesium oxide in Class C). The data from the two encapsulation runs were combined into one PLS model, which used 8 factors to achieve the fit shown ($r^2 = 0.995$), giving a SEP of 1.48 weight percent. The red and blue squares in Figure 4 correspond to the Class C and Class F cross-validation results, respectively. Once the model was created, additional TIRS spectra not included in the training set were analyzed as unknowns. These results are shown in the figure as red and blue circles. The rms error of the unknowns is 0.91 weight percent.

CONCLUSION

The data discussed shows that the TIRS monitor can provide accurate, real-time analysis of the composition of polyethylene-encapsulated waste streams. The TIRS monitor is a noncontact device that acquires mid-infrared spectra from a moving process stream. It has been demonstrated on DOE process lines encapsulating nitrate-salt LLMW and its surrogate, molten salt oxidation LLMW and its surrogate, and flyash. During the specific demonstrations discussed in this paper, the monitor achieved standard errors of prediction near 1% by weight.

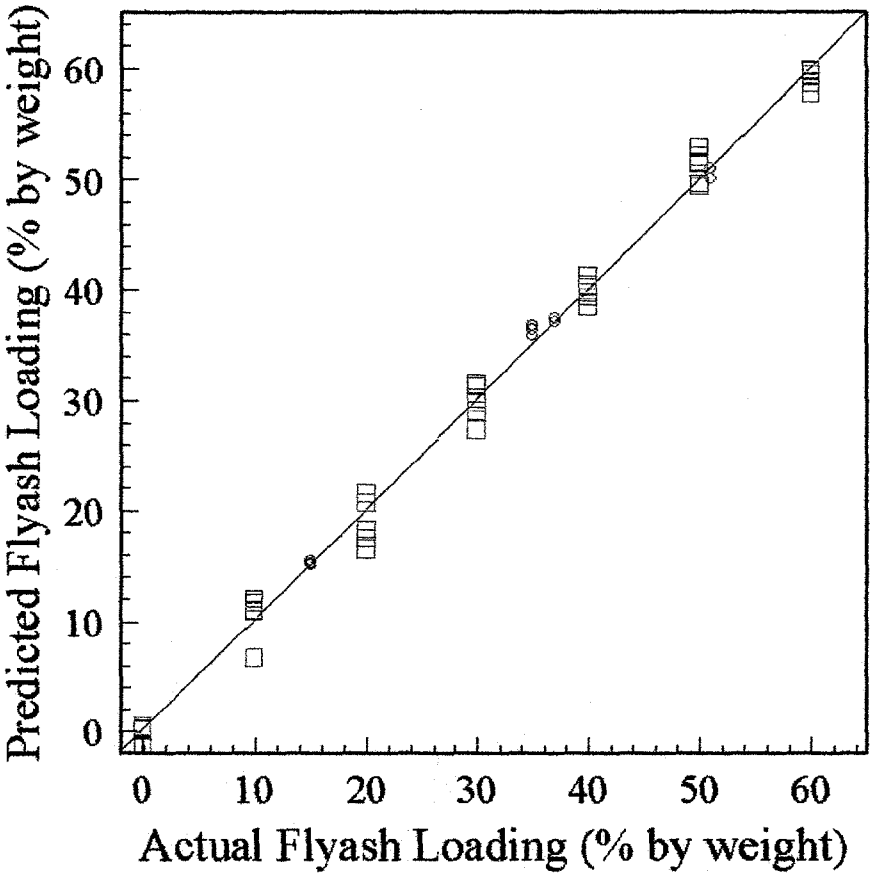

Fig. 4. Unknowns analysis and cross-validation correlation between TIRS predictions and actual compositions for flyash microencapsulated in polyethylene. Squares denote the cross validation data, and circles show the unknowns analysis. Red markers are for Class C flyash, and blue markers are for Class F.

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